Electronic Supplementary Material (ESI) for Lab on a Chip.

Supporting Information for

Nanocrystal Synthesis, µFluidic Sample Dilution and Direct Extraction of Single Emission Linewidths in Continuous Flow

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Experimental Section

Materials. Cadmium oxide (CdO, Sigma-Aldrich, ≥ 99.99 % trace metal basis), Selenium (Se, ~100 mesh, 99.99 % trace metals, Sigma-Aldrich) powder, oleic acid (OA, Sigma-Aldrich, 90 %), octadecene (ODE, Sigma-Aldrich, 90 %), decylamine (99 %, Sigma-Aldrich), Tri-n-octylphosphine (TOP, 97 %, Sigma-Aldrich) and toluene (99.5 %, anhydrous, Sigma-Aldrich).

Precursor preparation. Preparation of Cd-oleate stock solution: CdO (13 mg, 0.1 mmol) was loaded into a 200 mL Schlenk flask along with OA (3.2 mL) and ODE (96.8 mL). The mixture was degassed for 2 h at 110 °C and heated under N_2 to 190 °C until the solution turned clear. The solution was cooled and stored under nitrogen for several days at room temperature. Preparation of TOP-Se stock solution: Se powder (18 mg, 0.2 mmol) was dissolved in 4.5 mL TOP inside the glove box and the solution was sonicated till the complete dissolution of Se. Then the solution was further mixed with 95.5 mL ODE. Both precursor solutions were transferred to 25 mL glass gastight syringes (Hamilton Robotics) for the F-PCFS measurements.

Buffer preparation: 1.25 mL of ~ 0.1 M $Cd(OA)_2$ (solid at room temperature) in ODE was melted with a heat gun and it was mixed with 8.75 mL of toluene and 100 µL decylamine. The solution needs to be kept in the dark and ideally under N_2 to avoid autofluorescence from the buffer solution (it turns yellow after several weeks). For the in-line dilution of CdSe QDs we further diluted the stock solution in toluene with (1:5 volume ratio) for the preparation of a 30 mL buffer solution, which was then transferred into a plastic syringe for performing an F-PCFS measurement.

F-PCFS Setup. Flow-photon-correlation-Fourier-spectroscopy (F-PCFS) setup used to separate the ensemble averaged single NC linewidth from the ensemble linewidth. F-PCFS was performed using a home-built confocal microscope. CdSe QDs synthesized and diluted in-situ were excited (405 nm cw, Melles Griot), and the spatially (telescope with pinhole) and spectrally (425 nm LP optical filter, Thorlabs) filtered emission of typically between ~100 and 10000 NCs is directed into a Michaelson interferometer with a 50/50 beamsplitter. The path length difference is controlled by a linear encoded stage with controller (Newport). During the F-PCFS experiment, the center path-length difference is adjusted to discrete positions within the coherence length of the emission (typically between 60 and 90 µm) using step increments of typically ~ 250 nm. At each stage position, the path-length difference is dithered over approximately twice the center emission wavelength with typical frequencies of around 0.05 to 0.1 Hz, and the picosecond resolved photon-stream of both interferometer arms is recorded with single-photon counting modules (PerkinElmer SPCMs) and a picosecond photon counting card (HydraHarp, PicoQuant). We use home-built software (MATLAB) to obtain the second order photon cross-and auto-correlations at each stage-position and separate the average single NC spectral correlation from the ensemble. Ensemble emission spectra which are recorded using a highly sensitive cooled EMCCD camera after dispersion with a monochromator (both Princeton Instrument). We refer to our previous publications for a detailed description of the spectroscopic technique, and data analysis.[1-3]

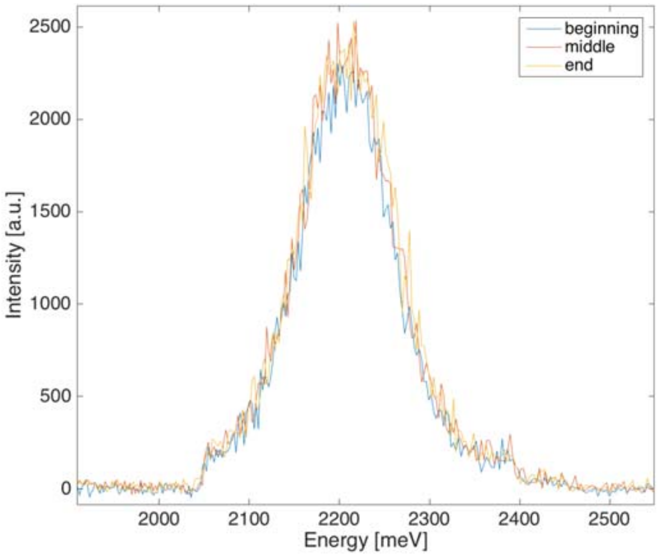

Figure S1: PL spectra of CdSe QDs extracted from at the beginning, middle, and end of the F-PCFS measurement. The reaction parameters were: T = 250 °C, reaction time = 3.5 minutes, Se:Cd = 1.5, Q_{QD}: Q_B = 2

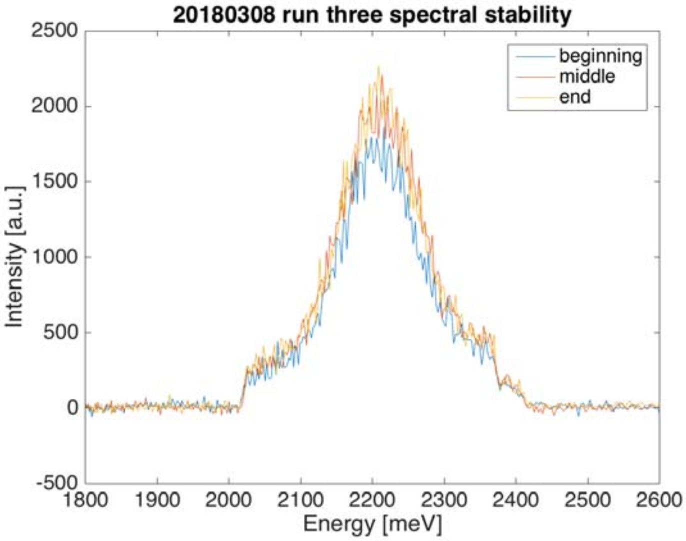

Figure S2: PL spectra of CdSe QDs extracted from at the beginning, middle, and end of the F-PCFS measurement. The reaction parameters were: T = 260 °C, reaction time = 3.5 minutes, Se : Cd = 1.5, Q_{QD} : Q_B = 1

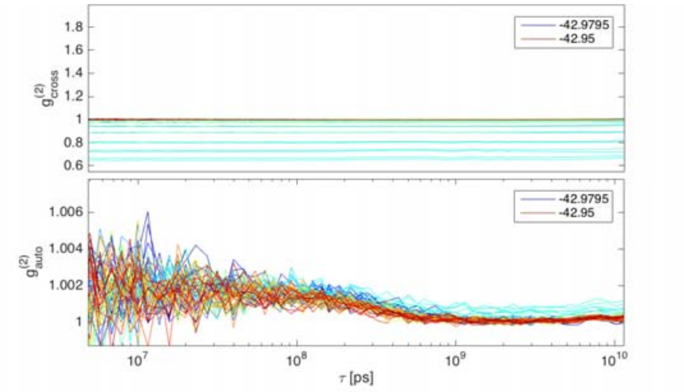

Figure S3: Auto- and cross correlation traces for CdSe QDs at different interferometer path-length differences. The synthesis conditions were: T = 250 °C, reaction time = 3.5 minutes, Se : Cd = 1.5, Q_{QD} : Q_B = 2.

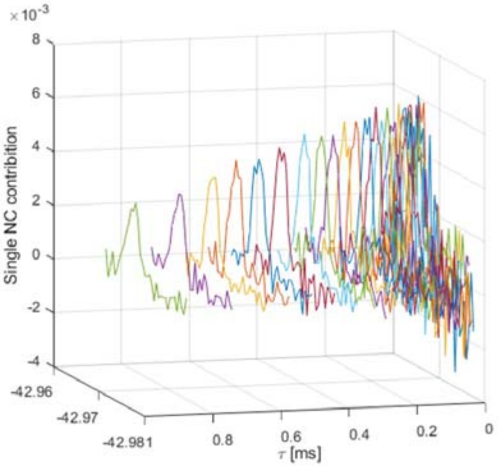

Figure S4: Single NC interferograms of CdSe QDs at various τ. The QDs were synthesized at T = 270 °C, reaction time = 3.5 minutes, Se : Cd = 1.5, Q_{QD} : Q_B = 2.

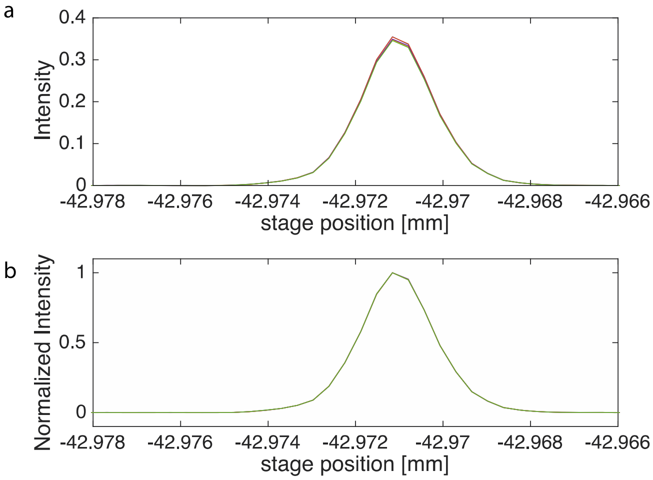

Figure S5: Single NC PCFS interferogram (non-normalized, a; normalized for clarity, b) for different τ illustrating the invariance of its shape. The QDs were synthesized at T = 270 °C, reaction time = 3.5 minutes, Se : Cd = 1.5, $Q_{QD} : Q_B = 2$.

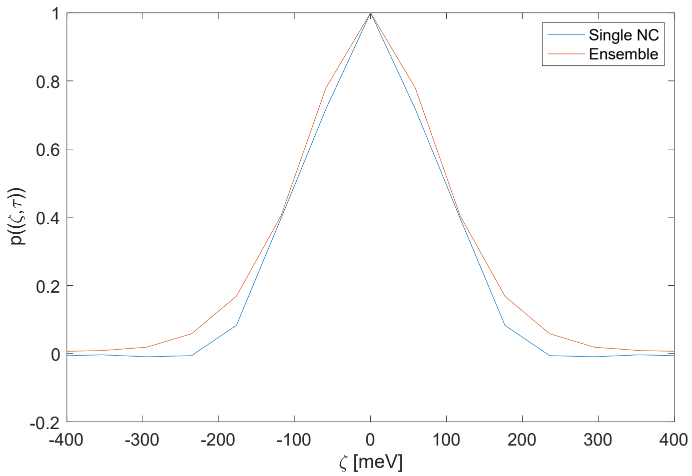

Figure S6: Ensemble averaged single NC (blue line) and ensemble spectral correlation (red line) for CdSe QDs synthesized at T = 250 °C, reaction time = 3.5 minutes, Se : Cd = 1.5, $Q_{QD} : Q_B = 2$.

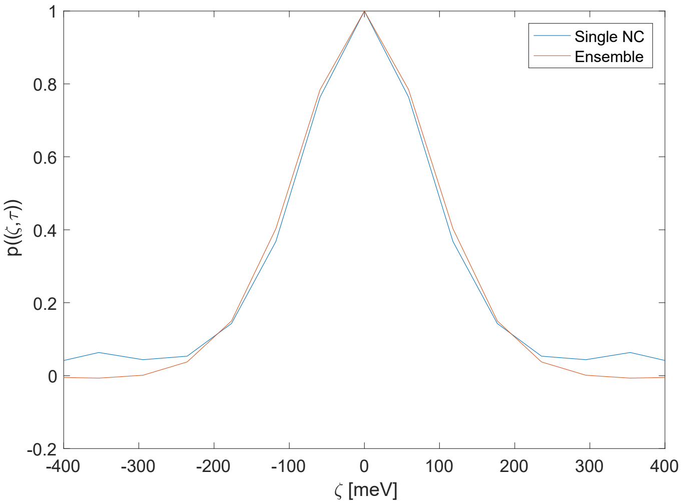

Figure S7: Ensemble averaged single NC (blue line) and ensemble spectral correlation (red line) for CdSe QDs synthesized at T = 260 °C, reaction time = 3.5 minutes, Se : Cd = 1.5, $Q_{QD} : Q_B = 1$.

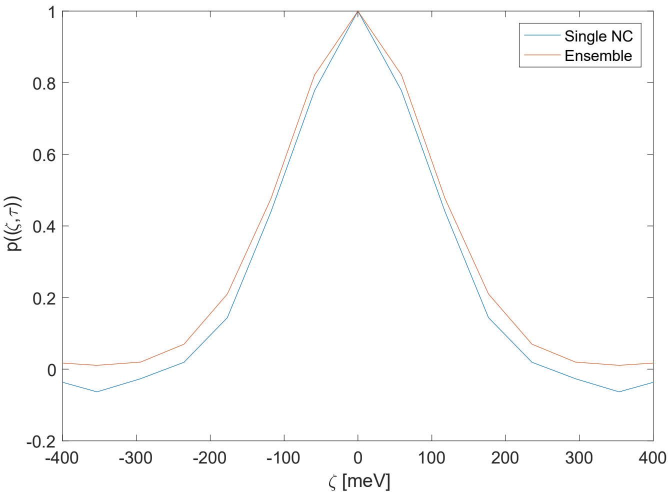

Figure S8: Ensemble averaged single NC (blue line) and ensemble spectral correlation (red line) for CdSe QDs synthesized at T = 270 °C, reaction time = 3.5 minutes, Se : Cd = 1, $Q_{QD} : Q_B = 1.4$.

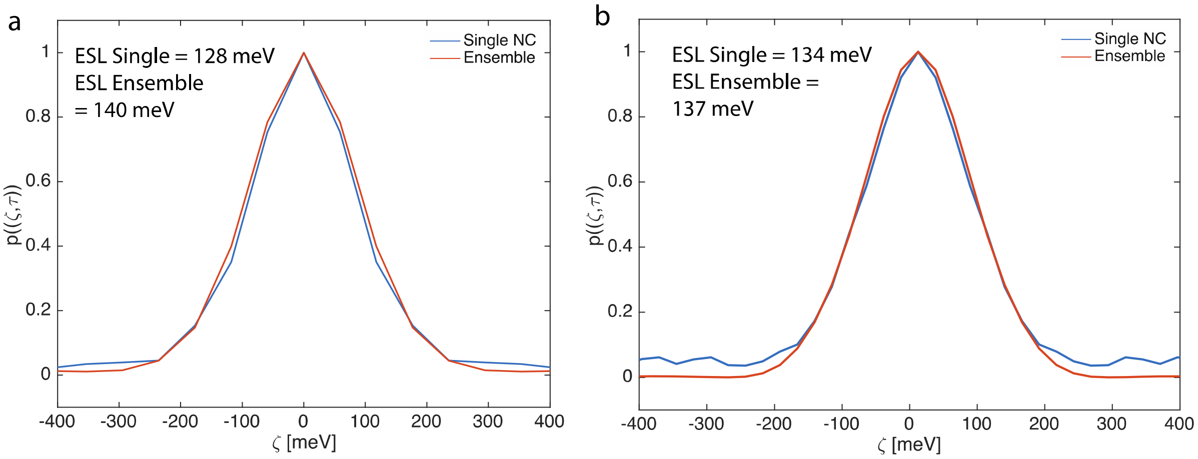

Figure S9: Ensemble averaged single NC (blue line) and ensemble spectral correlation (red line) for two batches of CdSe QDs synthesized at 270 °C, reaction time = 3.5 minutes, Se : Cd = 1.5, $Q_{QD} : Q_B = 2$. In both cases, the error for the effective spectral lineshape (ESL) is smaller than 5% of the absolute linewidth and is not attributed to the added complexity of the system owing to the flow functionality. Our results are, within error, reproducible and the final results presented in Figure 4 valid as the identified lineshape differences for different reaction conditions are larger than the margin of error for the spectroscopic setup.

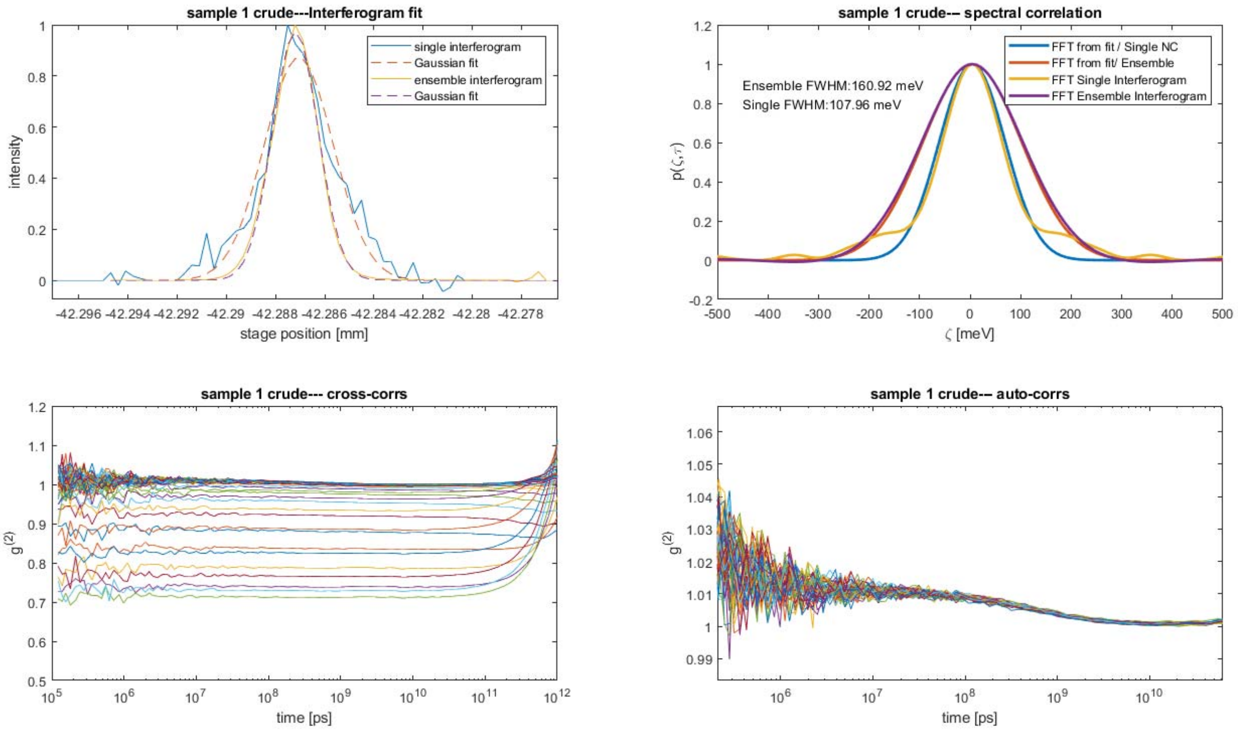

Figure S10: S-PCFS analysis of a crude solution (sample 1) of CdSe QDs synthesized in the microfluidic reactor. (Top left) Single and ensemble PCFS interferograms and their gaussian fits, (top right) ensemble averaged single NC and ensemble spectral correlation, (bottom left) cross correlation traces and (bottom right) auto-correlation traces. Synthetic parameters are: T = 280 °C, reaction time = 2 minutes, Se : Cd = 2.

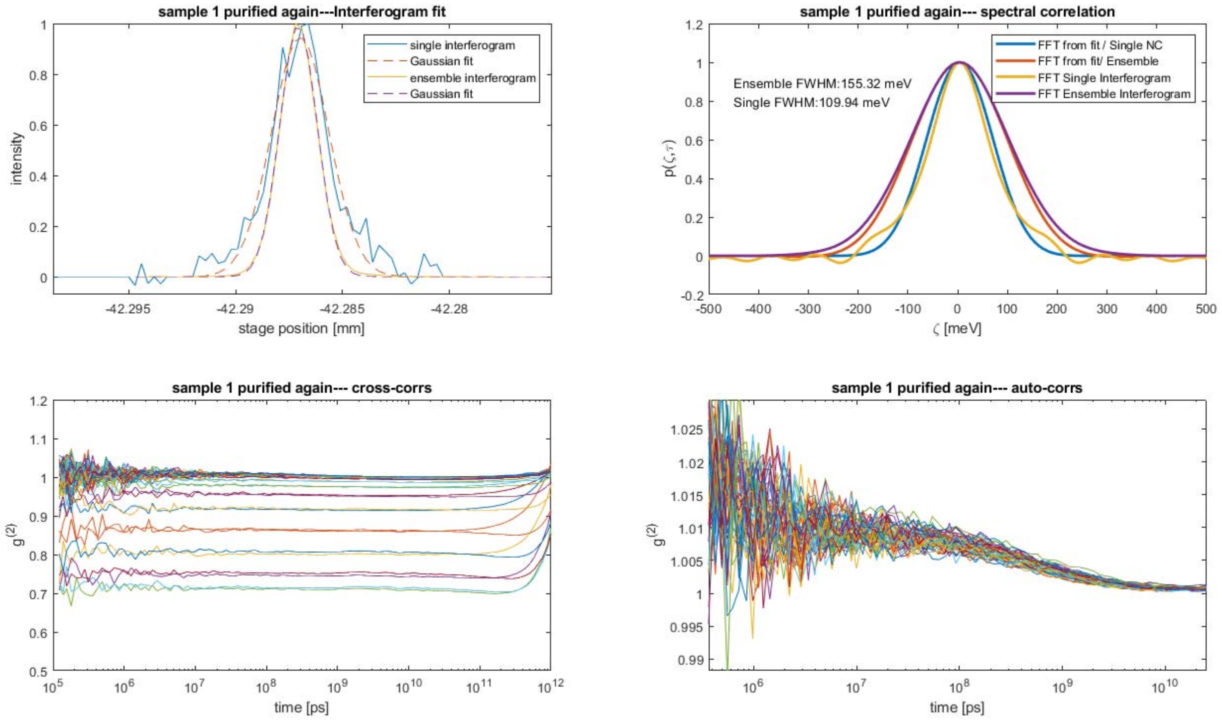

Figure S11: S-PCFS analysis of a purified solution (sample 1) of CdSe QDs synthesized in the microfluidic reactor. (Top left) Single and ensemble PCFS interferograms and their gaussian fits, (top right) ensemble averaged single NC and ensemble spectral correlation, (bottom left) cross correlation traces and (bottom right) auto-correlation traces. Synthetic parameters are: T = 280 °C, reaction time = 2 minutes, Se : Cd = 2. For particle purification, 2 mL of the crude solution (sample 1) were mixed with 6 mL of acetone and centrifuged at 7500 rpm for 5 min. Particles were then re-dispersed in toluene.

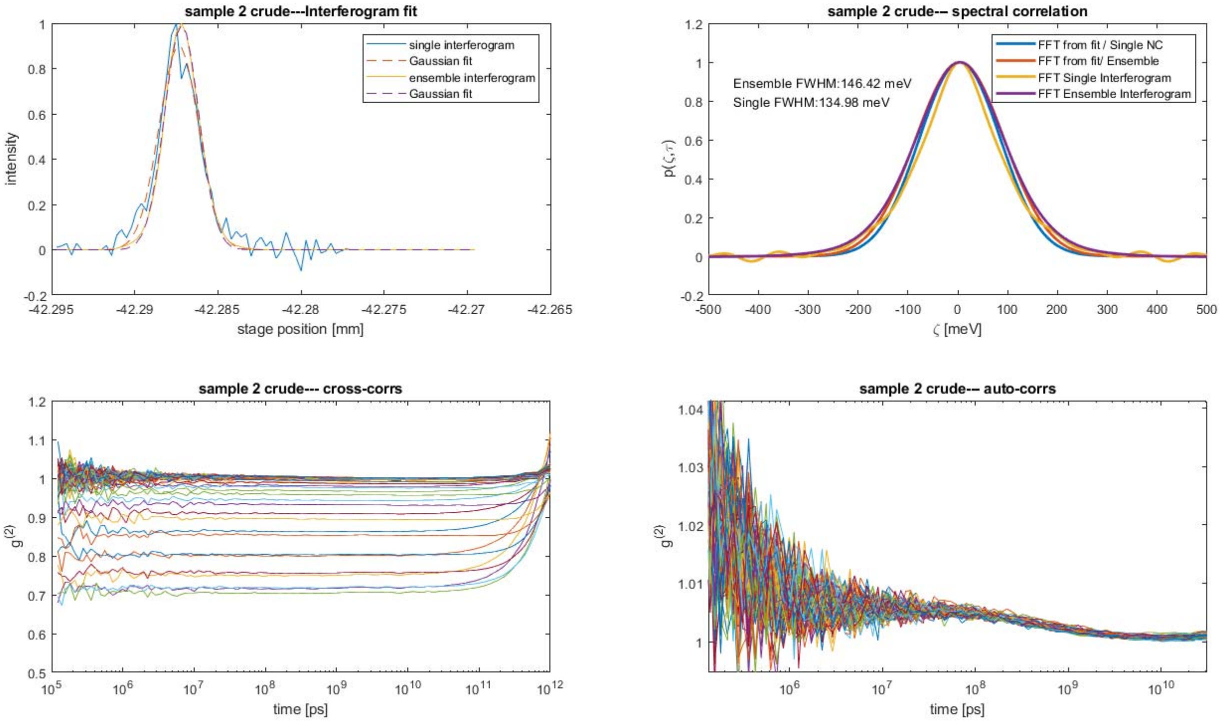

Figure S12: S-PCFS analysis of a crude solution (sample 2) of CdSe QDs synthesized in the microfluidic reactor. (Top left) Single and ensemble PCFS interferograms and their gaussian fits, (top right) ensemble averaged single NC and ensemble spectral correlation, (bottom left) cross correlation traces and (bottom right) auto-correlation traces. Synthetic parameters are: T = 300 °C, reaction time = 2 minutes, Se : Cd = 2.

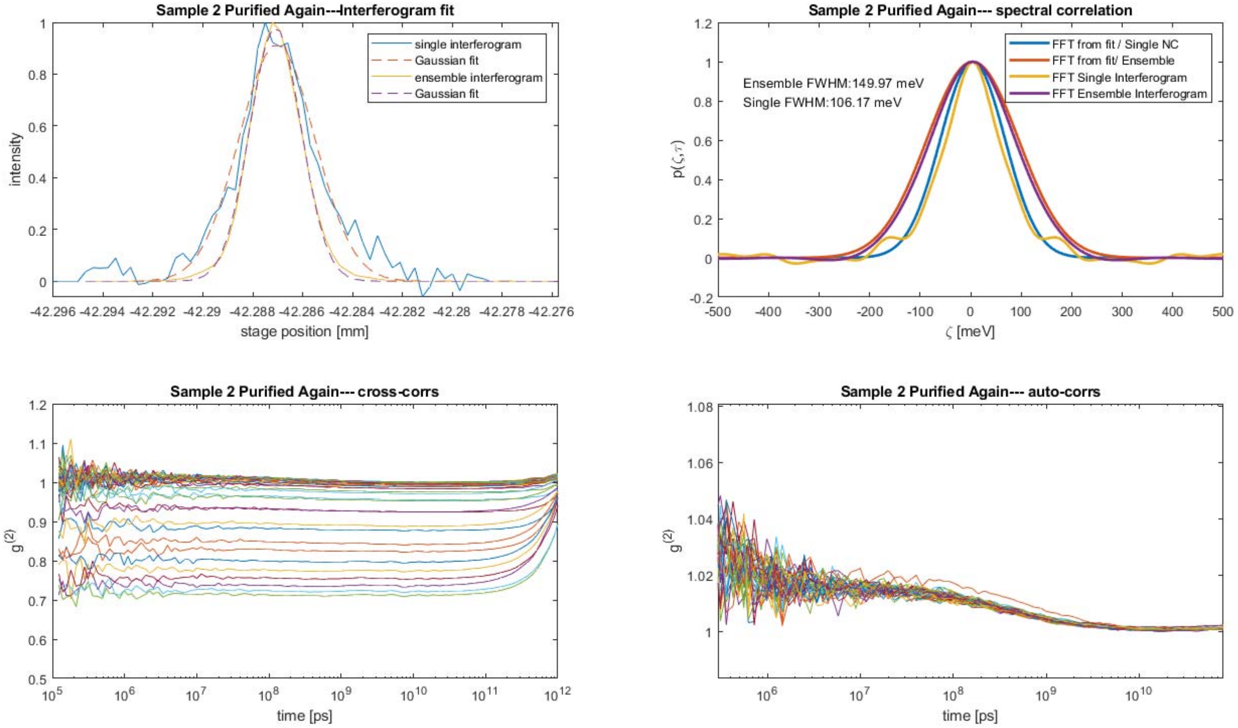

Figure S13: S-PCFS analysis of a purified solution (sample 2) of CdSe QDs synthesized in the microfluidic reactor. (Top left) Single and ensemble PCFS interferograms and their gaussian fits, (top right) ensemble averaged single NC and ensemble spectral correlation, (bottom left) cross correlation traces and (bottom right) auto-correlation traces. Synthetic parameters are: T = 300 °C, reaction time = 2 minutes, Se : Cd = 2. For particle purification, 1 mL of the crude solution (sample 1) were mixed with 5 mL of acetone and centrifuged at 7500 rpm for 5 min. Particles were then re-dispersed in toluene.

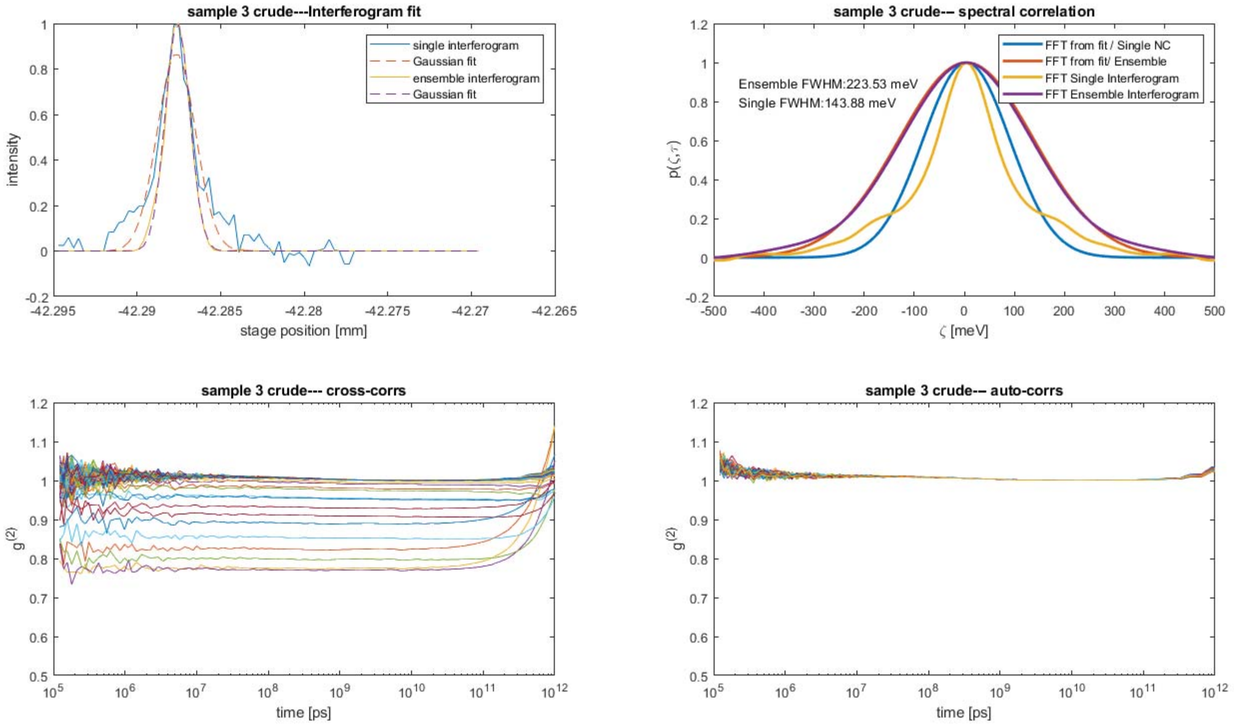

Figure S14: S-PCFS analysis of a crude solution (sample 3) of CdSe QDs synthesized in the microfluidic reactor. (Top left) Single and ensemble PCFS interferograms and their gaussian fits, (top right) ensemble averaged single NC and ensemble spectral correlation, (bottom left) cross correlation traces and (bottom right) auto-correlation traces. Synthetic parameters are: T = 300 °C, reaction time = 2 minutes, Se : Cd = 1.

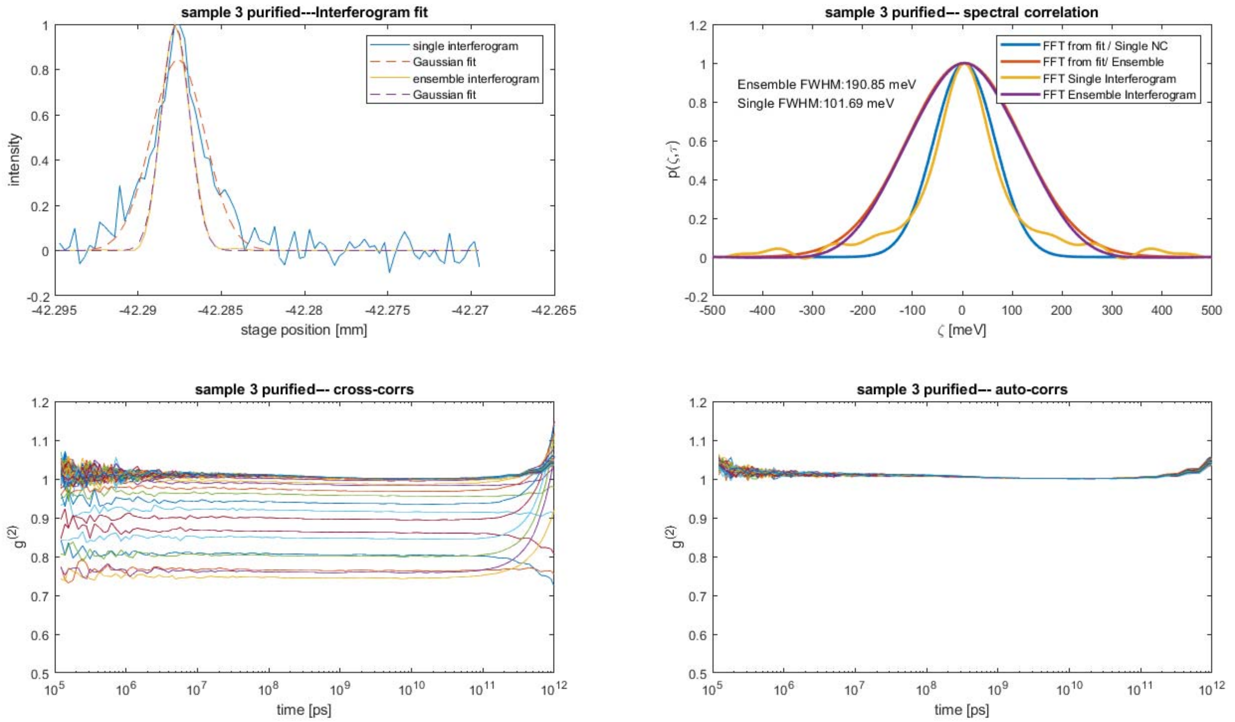

Figure S15: S-PCFS analysis of a purified solution (sample 1) of CdSe QDs synthesized in the microfluidic reactor. (Top left) Single and ensemble PCFS interferograms and their gaussian fits, (top right) ensemble averaged single NC and ensemble spectral correlation, (bottom left) cross correlation traces and (bottom right) auto-correlation traces. Synthetic parameters are: T = 300 °C, reaction time = 2 minutes, Se : Cd = 1. For particle purification, 1 mL of the crude solution (sample 1) were mixed with 5 mL of acetone and centrifuged at 7500 rpm for 5 min. Particles were then re-dispersed in toluene.

Table S1: Summary of $\text{ESL}_{\text{single}}$ and $\text{ESL}_{\text{ensemble}}$ of crude and purified solutions after conducting S-PCFS measurements.

	Crude Ensemble [meV]	**Crude Single [meV]**	**Purified Ensemble [meV]**	**Purified Single [meV]**
Sample 1	160	107	155	109
Sample 2	146	134	149	106
Sample 3	223	143	190	101

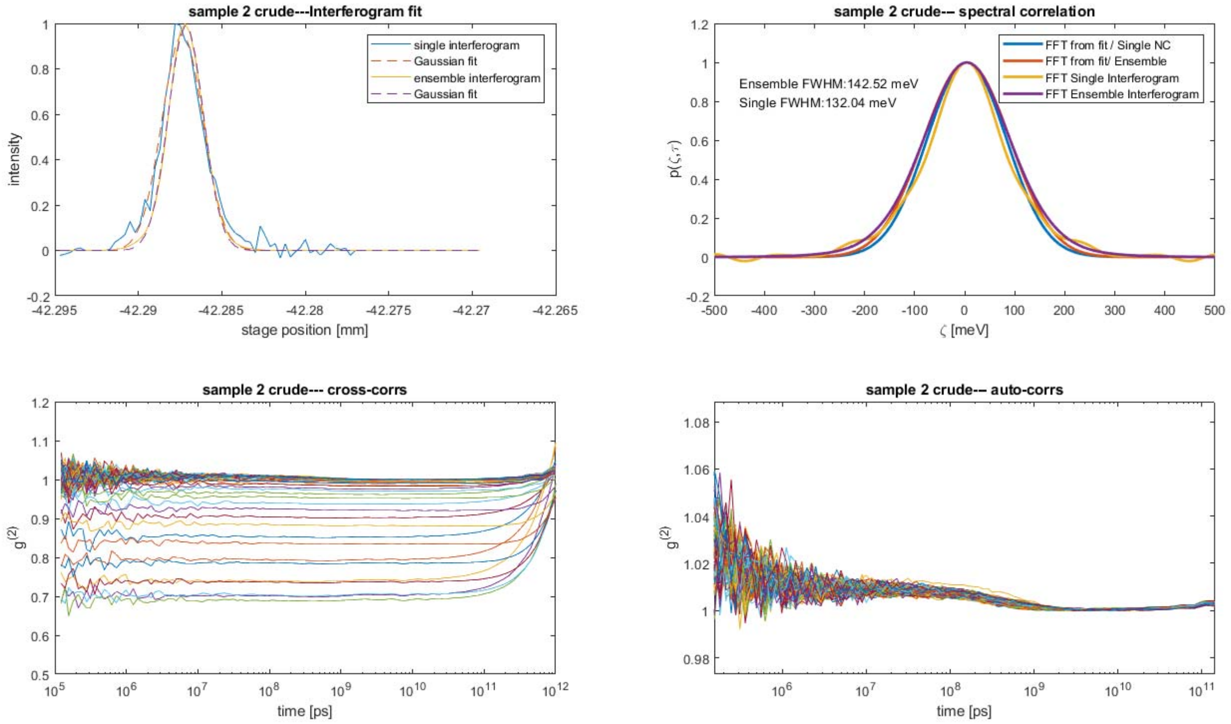

Figure S16: F-PCFS analysis of a crude solution (sample 3) of CdSe QDs synthesized in the microfluidic reactor. (Top left) Single and ensemble PCFS interferograms and their gaussian fits, (top right) ensemble averaged single NC and ensemble spectral correlation, (bottom left) cross correlation traces and (bottom right) auto-correlation traces. Synthetic parameters are: T = 300 °C, reaction time = 2 minutes, Se : Cd = 2. The crude solution was diluted and then loaded into a syringe for the F-PCFS measurements.

References

1. J. Cui, A. P. Beyler, L. F. Marshall, O. Chen, D. K. Harris, D. D. Wanger, X. Brokmann and M. G. Bawendi, *Nat Chem*, 2013, **5**, 602-606.
2. J. Cui, A. P. Beyler, I. Coropceanu, L. Cleary, T. R. Avila, Y. Chen, J. M. Cordero, S. L. Heathcote, D. K. Harris, O. Chen, J. S. Cao and M. G. Bawendi, *Nano Lett*, 2016, **16**, 289-296.
3. J. R. Caram, S. N. Bertram, H. Utzat, W. R. Hess, J. A. Carr, T. S. Bischof, A. P. Beyler, M. W. B. Wilson and M. G. Bawendi, *Nano Lett*, 2016, **16**, 6070-6077.